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Review of New Source Performance Standards for Phosphate Fertilizer Industry - Revised

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16. ABSTRACT

Since promulgation of new source performance standards (NSPS) for fluoride control in the phosphate fertilizer industry, in 1975, commercial applications of a few new systems that reduce air pollution from phosphate plants have been reported. These include scrubbing system modifications that reduce the size of ponds used to cool process water, and reduce pond fluoride emissions. Also, a proprietary new process produces a stable granular triple superphosphate (GTSP) directly. This process reduces or eliminates the emissions of fluorides and fugitive particulate during the curing, storage period. The new GTSP process also eliminates the scrubbing of certain process gas, thus reducing required cooling pond area and pond fluoride emissions. There is currently insufficient process experience and source test data for firm conclusions about fluoride control potential. The recommendation is therefore made not to develop NSPS revisions now, but to assess additional developments in this industry in four years, and then reconsider possible revision.

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Review of New Source Performance Standards for Phosphate Fertilizer Industry — Revised

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

November 1980

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1. INTRODUCTION

1.1 PURPOSE AND SCOPE

On August 6, 1975, the Environmental Protection Agency promulgated New Source Performance Standards (NSPS) for Five Catagories of Sources in the Phosphate Fertilizer Industry (40 FR 33152). These standards establish emissions limits and require emission testing and reporting for total fluorides from wet process phosphoric acid (WPPA) plants, superphosphoric acid (SPA) plants, diammonium phosphate (DAP) plants, triple superphosphate (TSP) plants, and granular triple superphosphate (GTSP) storage facilities.

The Clean Air Act Amendments of 1977 require that the Administrator of the EPA review and, if appropriate, revise established standards of performance for new stationary sources at least every four years (Section 111(b)(1)(B)). This report includes reviews of recent growth of the phosphate fertilizer industry. Changes in process technology since 1975 are presented, and advances in the control of fluorides from gypsum ponds are discussed. Inquiries were made on enforcement problems of the current NSPS and on continuous monitoring of fluoride control devices, and the results are presented. Compliance test results; information from the literature; and discussions with representatives of industry, control equipment vendors, phosphate fertilizer plant designers, EPA regional offices, state agencies, and the Tennessee Valley Authority form the basis for these reviews. The information obtained was analyzed to determine whether potential benefits exist that would warrant NSPS revision now.

1.2 STUDY RESULTS

Based on results of this investigation, conclusions were drawn on significant developments in the phosphate industry since NSPS promulgation, and recommendations were formulated on action to be taken pertaining to NSPS revision. These conclusions and recommendations are shown in Section 7 of this report.

2. INDUSTRY GROWTH

2.1 PRODUCTION CAPACITY

The total capacity of plants in the U.S. for production of wet process phosphoric acid (WPPA), superphosphoric acid (SPA), ammonium phosphate (AP), and triple superphosphate (TSP), for the years beginning 1974 is shown in Table 2-1. The Table 2-1 values were derived from TVA compilations.[1] This data source was supported by recommendation of the Fertilizer Institute.[2]

Table 2-1 shows that production capacity increased for WPPA, SPA, AP, and TSP, during the years 1974 through 1979, by 3071, 496, 955, and 313 thousand tons P_2O_5, respectively. This amounts to an average annual growth of 614, 99, 191 and 63 thousand tons P_2O_5 for each product, respectively, over those 5 years. This growth was due both to construction of some new units, and de-bottlenecking.

Table 2-1 also shows that the projected capacity increases for those products from 1979 to 1980 are 461, 350, 0, and 0, respectively.

For 1980 through 1985, there is expected to be a small to moderate capacity increase for all aforementioned products.

Recent literature indicates that U.S.-located phosphate plants are now producing at nearly full capacity due largely to high export demand; but that further expansion would be contingent on continued current export levels and increased domestic demand - conditions not assured. Exports might be reduced because of potential high production outside the U.S.[3,4,5] Pertaining to domestic demand, U.S. and Puerto Rican phosphate use decreased 9% in 1978; and there are strong indications that some soils have been overfertilized with phosphate.[6,7] These factors support the expectation of decreased rates of expansion of phosphate production capacity in the U.S. between 1980 and 1985.

TABLE 2-1. PHOSPHATE PRODUCTION CAPACITY IN THE U.S. (THOUSAND SHORT TONS P_2O_5)[1]

Product	1974	1975	1976	1977	1978	1979	1980
Phosphoric acid (WPPA)	6680	8518	9001	9346	9601	9751	10212
Superphosphoric acid	747	877	1012	1037	893	1243	1593
Ammonium phosphate[a]	3806	4548	4721	5267	4794	4761	4761
Concentrated (triple) Superphosphate[b]	2127	2367	2596	2440	2440	2440	2440

[a] Includes monoammonium phosphate and diammonium phosphate.

[b] Includes run-of-pile and granulated triple superphosphate.

2.2 REFERENCES FOR SECTION 2.

1. Tennessee Valley Authority. World Fertilizer Capacity: "Phos Acid WP," TVA-05/10/79; "Super Acid W," TVA-05/21/79; "AM Phosphate," TVA-05/21/79; "Conc Super," TVA-05/21/79. Muscle Shoals, Alabama. 22 p.

2. Letter from K.T. Johnson, The Fertilizer Institute, to W.O. Herring, U.S. EPA. April 18, 1979. Subject: Phosphate Industry in U.S.

3. Key Chemicals, Phosphoric Acid. Chemical and Engineering News. p. 18. April 30, 1979.

4. 1979 Fertilizer Situation. U.S. Dept. of Agriculture. Washington, D.C. Publication FS-9. Dec. 1978. p. 23.

5. Harris, G.T., and E.A. Harre. World Fertilizer Situation and Outlook - 1978-85. International Fertilizer Development Center and Tennessee Valley Authority. Muscle Shoals, Alabama 35660. Bulletin IFDC-T-13, March 1979. pp. 8-13.

6. Reference 4, p. 11.

7. Situation 78 - TVA Fertilizer Conference. Tennessee Valley Authority. Muscle Shoals, Alabama 35660. Bulletin Y-131. Aug. 1978. p. 54.

3. PRODUCTION PROCESS CHANGES

All processes used commercially to make wet process phosphoric acid, superphosphoric acid, diammonium phosphate, and triple superphosphate are summarized in Sections 3.1 through 3.5, below. Changes of production process application since NSPS publication in August 1975, are identified and discussed in Section 3.6. The status of potential regulation of radioactive emissions from phosphate plants is given in Section 3.7.

3.1 WET PROCESS PHOSPHORIC ACID

3.1.1 Dihydrate Processes

Wet process phosphoric acid (WPPA) is made by reacting sulfuric acid (H_2SO_4) with fluorapatite ($Ca_{10}(PO_4)_6F_2$) in phosphate rock. In the dihydrate processes, calcium sulfate, as the dihydrate, gypsum ($CaSO_4 \cdot 2H_2O$), is also formed. The overall reaction is described by the following equation:[1]

$$3\ Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \rightarrow 30CaSO_4 \cdot 2\ H_2O + 18H_3PO_4 + H_2SiF_6$$

Calcium sulfate precipitates, and the liquid phosphoric acid is separated by filtration. A modern dihydrate, WPPA plant flow diagram is shown in Figure 3-1.

Finely ground phosphate rock is continuously metered into the reactor and sulfuric acid is added. The single-tank reactor (Dorr-Oliver design) illustrated in Figure 3-1 consists of two concentric cylinders. Reactants are added to the annulus and digestion occurs in this outer compartment. The second (central) compartment provides retention time for gypsum crystal growth and prevents short-circuiting of rock.

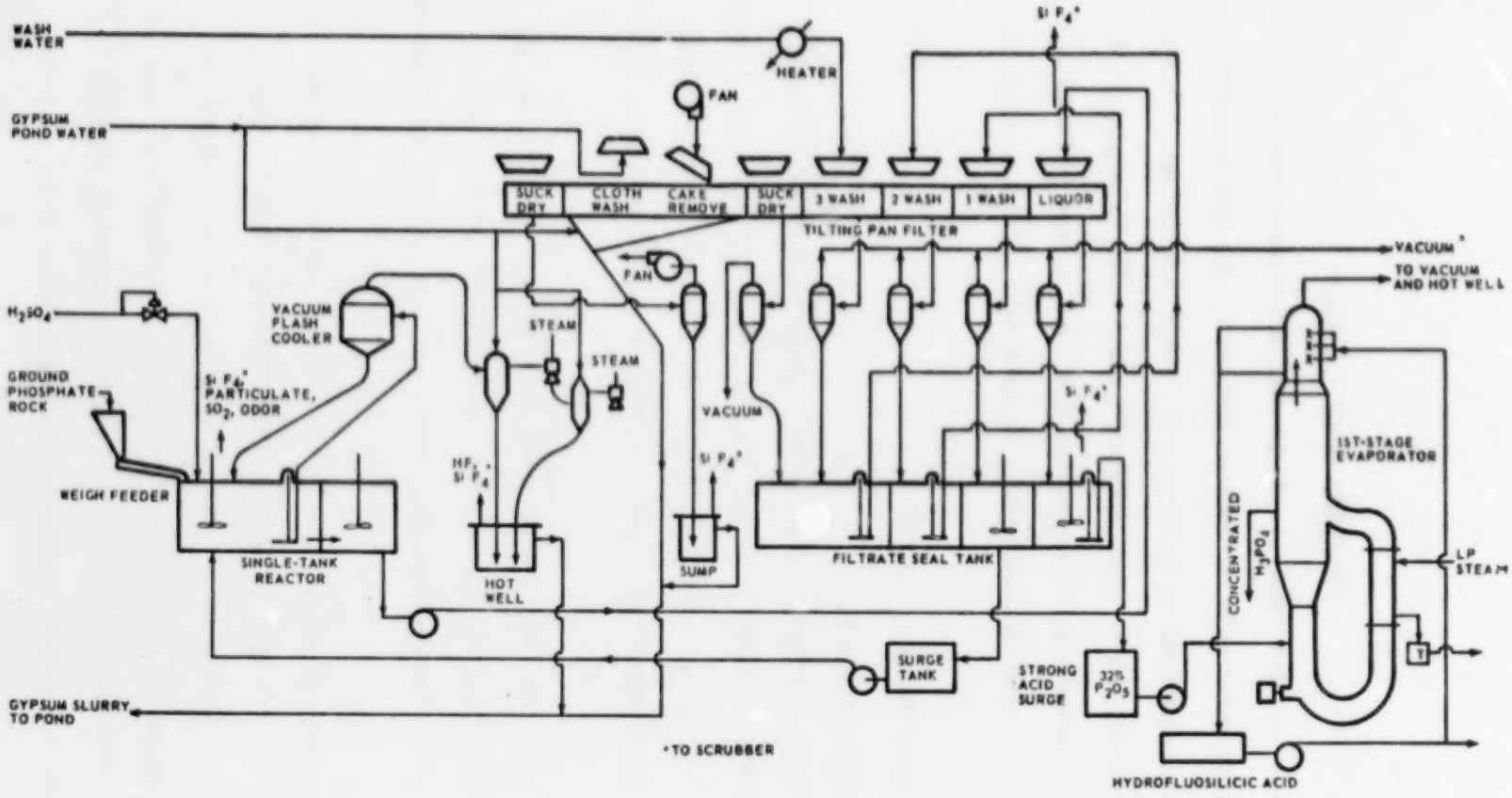

Figure 3-1. Flow diagram illustrating dihydrate wet-process phosphoric acid process.

Concentrated sulfuric acid is usually fed to the reactor. The only other water entering the reactor is the filter-wash water.

Considerable heat of reaction is generated in the reactor and must be removed. This heat removal is done in modern plants by vacuum-flash-cooling part of the slurry and sending it back into the reactor.

The reaction slurry is held in the reactor for up to 8 hours before being sent to the filter. The most common filter design is the rotary horizontal tilting-pan vacuum filter denoted in Figure 3-1. It consists of a series of individual filter cells mounted on a revolving annular frame.

Product slurry from the reactor is introduced into a filter cell and vacuum is applied. After a dewatering period, the filter cake undergoes two or three stages of washing with progressively weaker solutions of phosphoric acid. The wash-water flow is countercurrent to the rotation of the filter cake with heated fresh water, or barometric condenser water, used for the last wash; the filtrate from this step is used as the washing liquor for the preceding stage, etc.

After the last washing, the cell is subjected to a cake dewatering step and then inverted to discharge the gypsum. Cleaning of the filter media occurs at this time. The cell is then returned to its upright position and begins a new cycle.

The 32 percent P_2O_5 acid obtained from the filter generally is concentrated to 54% in a two- or three-stage vacuum evaporator system. In the evaporator, illustrated in Figure 3-1, provision is made for recovery of fluoride as fluosilicic acid. Inclusion of this recovery feature depends on economics. Many evaporation plants do not have this device.

3.1.2 Hemihydrate (Hemidihydrate) Processes

Commercial hemihydrate, or hemidihydrate (HDH), processes for making phosphoric acid are distinquished from dihydrate processes by inclusion of two main stages - the hemihydrate stage, or first stage; and the dihydrate stage, or second stage. Fluoride recovery can be co-installed with the HDH process.[2]

Hemihydrate Stage

In the hemihydrate stage, phosphate rock is reacted with a mixture of 98% sulfuric acid and return phosphoric acid (from the hemihydrate filter) to yield phosphoric acid and calcium sulfate hemihydrate.[2] The overall reaction is represented by the equation:

$$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 13H_2O \rightarrow 30CaSO_4 \cdot 1/2H_2O + 18H_3PO_4 + H_2SiF_6$$

Relatively high temperatures and P_2O_5 concentrations are required to obtain calcium sulfate as hemihydrate, instead of dihydrate, in the reaction of fluorapatite with H_2SO_4.[3]

The resulting slurry is filtered to obtain the hemihydrate residue and phosphoric acid filtrate. Hemihydrate crystallization permits easier filtration, compared with dihydrate crystallization, requiring less water to dilute the acid for satisfactory filtration. Therefore, the acid obtained directly from filtration in the hemihydrate stage contains 40 to 54% P_2O_5, and is suitable as the finished product WPPA, without further concentration by evaporation.[2]

Dihydrate Stage

In the dihydrate stage, with further H_2SO_4 addition, the hemihydrate is recrystalized as the dihydrate. Co-precipitated lattice P_2O_5 is released from the hemihydrate precipitate during recrystallization. The dihydrate slurry is filtered with one or two wash stages. Filtrate, from the first wash stage, is recycled to the hemihydrate filter to recover the released P_2O_5.[2]

Fluoride Recovery

Fluorides are evolved from the reactors in both the hemihydrate and dihydrate stages, and from the flash cooler, in the hemihydrate stage. These fluorides can be recovered by means of a co-installed scrubbing system as byproduct H_2SiF_6.[2]

3.2 SUPERPHOSPHORIC ACID

Superphosphoric acid (SPA) is produced by submerged combustion or vacuum evaporation of clarified WPPA (containing 54% P_2O_5) to a P_2O_5 concentration between 72 and 76%. Vacuum evaporation is, commercially, much the more important method.[4]

There are two commercial processes for the production of superphosphoric acid by vacuum evaporation:

1. The falling film evaporation process (Stauffer Chemical Co.)
2. The forced circulation evaporation process (Swenson Evaporator Co.)

Feed acid clarification in both processes is usually accomplished by settling or by a combination of aging and settling. In general, both processes are also similar in other operations.

Figure 3-2 shows the Stauffer process. Feed acid is added to the evaporator recycle tank, where it mixes with concentrated product acid to maintain a highly concentrated process acid for lower corrosion rates. This mixture is pumped to the top of the evaporator and distributed to the inside wall of the evaporator tubes. The acid film moves down along the inside wall of the tubes receiving heat from the steam on the outside. Evaporation occurs and the concentrated acid is separated from the water vapor in a flash chamber located at the bottom of the evaporator. Product acid flows to the evaporator recycle tank and vapors to the barometric condenser. To minimize P_2O_5 loss, the separator section contains a mist eliminator to reduce carryover to the condenser.

3.3 DIAMMONIUM PHOSPHATE

Diammonium phosphate (DAP) is made in the reaction:

$$2\ NH_3 + H_3PO_4 \rightarrow (NH_4)_2\ HPO_4$$

It contains 18 percent nitrogen and 46 percent available P_2O_5. The TVA process for DAP production is the one in widest use, and there are several variations of the original now in use. A flow diagram of the basic process is shown in Figure 3-3.[5]

Anhydrous ammonia and phosphoric acid (about 40 percent P_2O_5) are reacted in the preneutralizer using a NH_3 / H_3PO_4 mole ratio of 1.35, which allows evaporation to a water content of 18 to 22 percent without thickening the DAP slurry to a nonflowing state. The slurry flows into the ammoniator-granulator and is distributed over a bed of recycled

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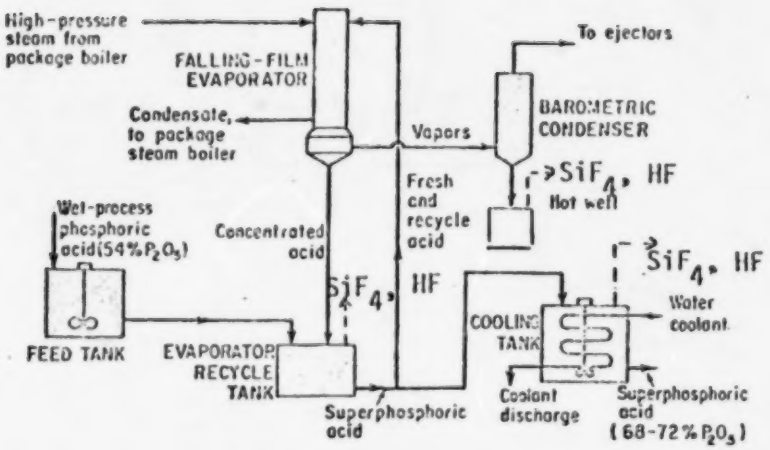

Figure 3-2. Stauffer superphosphoric acid process.

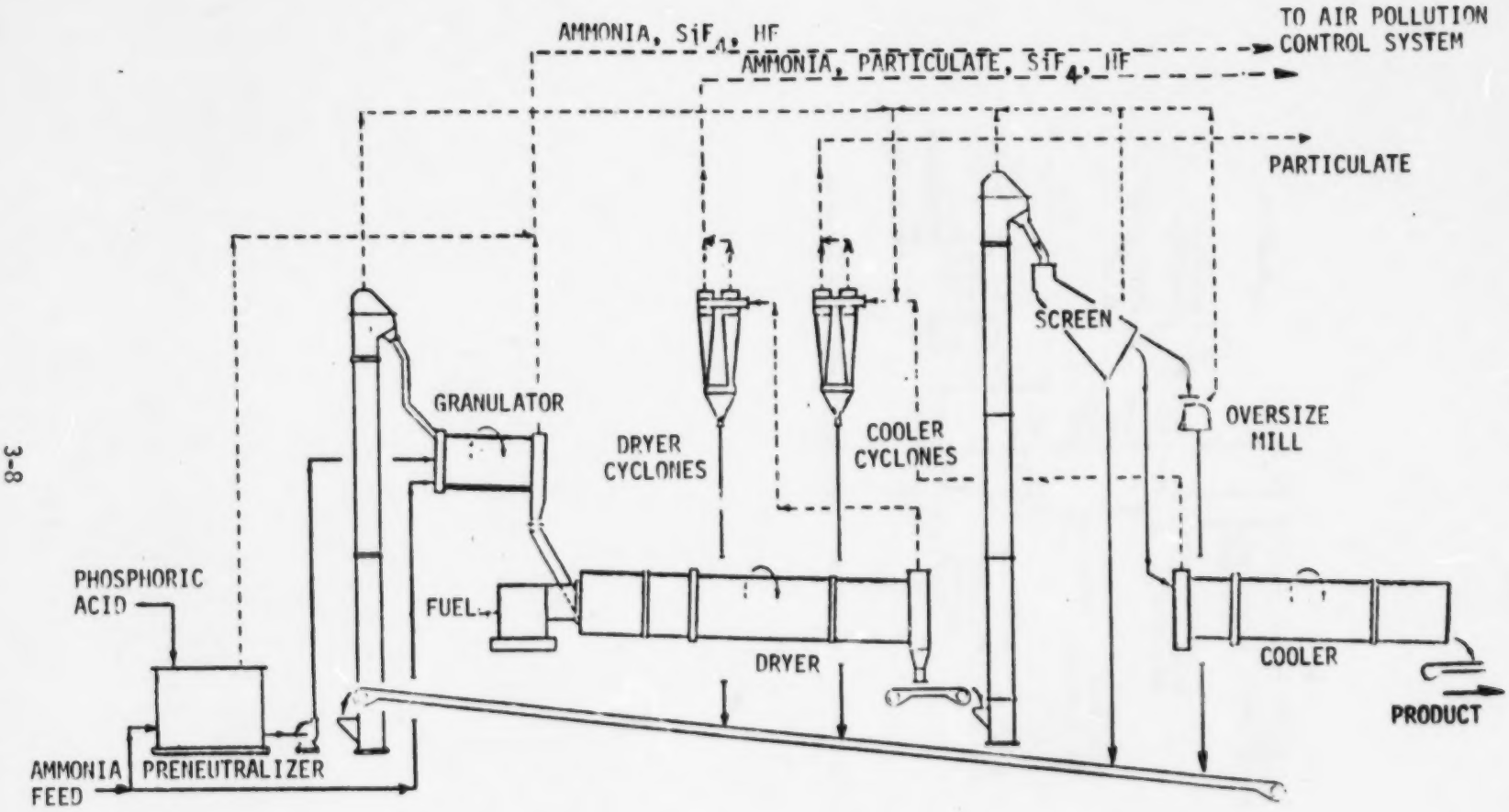

Figure 3-3. TVA diammonium phosphate process.

fines. Ammoniation to the required mole ratio of 2.0 takes place in the granulator by injecting ammonia under the rolling bed of solids. It is necessary to feed excess ammonia to the granulator to achieve a 2.0 mole ratio. Excess ammonia and water vapor driven off by the heat of reaction are directed to a scrubber, which uses phosphoric acid as the scrubbing liquid. The ammonia is almost completely recovered by the phosphoric acid scrubbing liquid and is recycled to the preneutralizer. Solidification occurs rapidly once the mole ratio has reached 2.0, making a low solids recycle ratio feasible.

Granulated DAP is next sent to the drier, then screened. Undersized and crushed oversized material are recycled to the granulator. Product sized material is cooled and sent to storage.

3.4 TRIPLE SUPERPHOSPHATE (TSP)

3.4.1 TSP from Phosphate Rock Treatment

Triple superphosphate (TSP), also called concentrated superphosphate, is made from phosphate rock in the reaction:

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10\ CaH_4(PO_4)_2 \cdot H_2O + 2HF$$

The product contains from 44 - 47 percent available P_2O_5.[6]

3.4.1.1 Run-of-Pile Triple Superphosphate - Figure 3-4 is a schematic diagram of the den process for the manufacture of run-of-pile (ROP) TSP. Phosphoric acid containing 52 - 54 percent P_2O_5 is mixed at ambient temperature with ground phosphate rock, usually in a TVA cone mixer. Mixing is accomplished by the swirling action of rock and acid streams introduced simultaneously into the cone. The chemical reaction begins during mixing.[6]

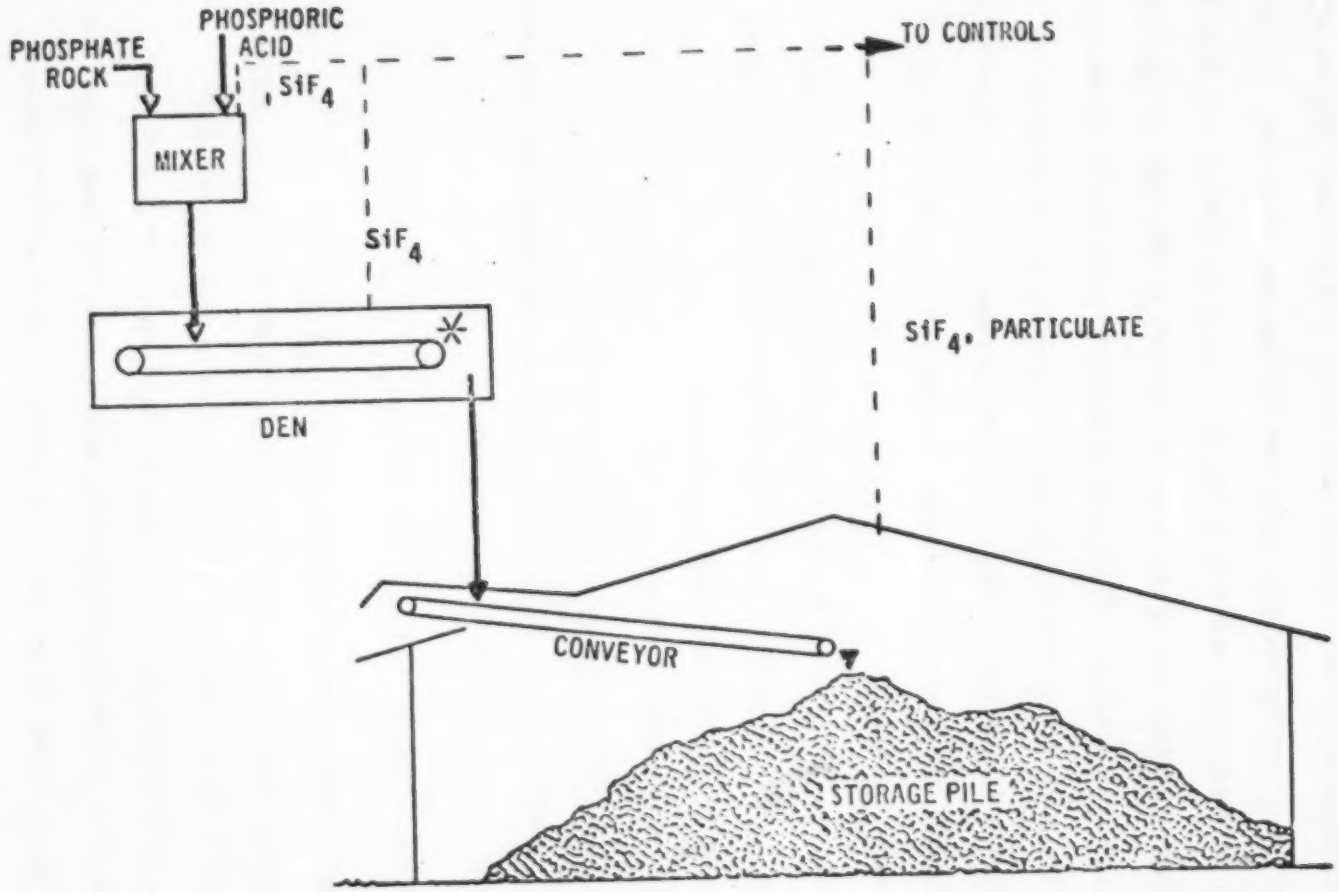

Figure 3-4. Run-of-pile triple superphosphate production and storage.

After mixing, the slurry goes to a "den," where solidification occurs. One of the most popular den designs is the Broadfield, a linear horizontal slat belt conveyor mounted on rollers with a long stationary box mounted over it and a revolving cutter at the end. The sides of the stationary box serve as retainers for the slurry until it sets.

The solidified slurry from the den must be cured - usually for 3 weeks or more - to allow the reactions to approach completion. Final curing occurs during sheltered storage, illustrated in Figure 3-4.

3.4.1.2 Granular Triple Superphosphate - Granular triple superphosphate (GTSP) is made from cured ROP TSP by treatment with water and steam in a rotary drum, then drying and screening.

The TVA one-step granular process, shown in Figure 3-5, makes GTSP directly. Ground phosphate rock and recycled process fines are fed into the acidulation drum along with concentrated phosphoric acid and steam. The use of steam helps accelerate the reaction and ensure an even distribution of moisture in the mix. The mixture is discharged into the granulator, where it solidifies, passes through a rotary cooler, and is screened. Over-sized material is crushed and returned with undersized material to the process.[6]

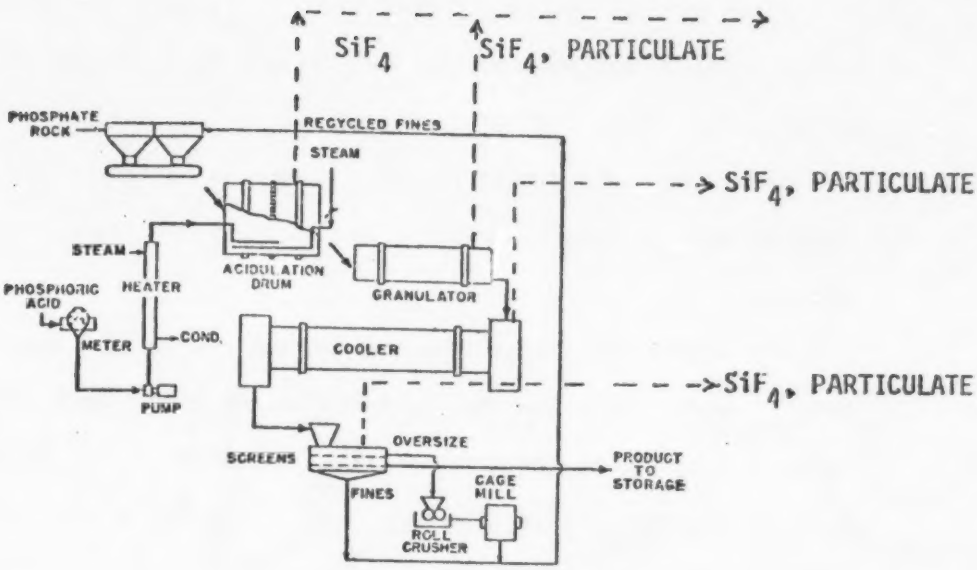

Figure 3-5. TVA one-step process for granular triple superphosphate.

The Dorr-Oliver slurry granulation process also produces GTSP directly. Ground phosphate rock is mixed with phosphoric acid (39% P_2O_5) in a series of mixing tanks. A thin slurry is continuously removed, mixed with a large quantity of dried, recycled fines in a pugmill mixer (blunger), where it coats out on the granule surfaces and builds up the granule size. The granules are dried, screened, and mostly (about 80 percent) recycled back into the process. Emissions from the drier and screening operations are sent to separate cyclones for dust removal and collected material is returned to the process.[6]

After manufacture, GTSP is stored for a short curing period. After storage of usually 3 to 5 days, during which some fluorides evolve from the storage pile, the product is considered cured. Front-end loaders move the GTSP to elevators or hoppers, where it is conveyed to screens for size separation. Oversize material is rejected, pulverized, and returned to the screen. Undersize material is returned to the GTSP production plant. Material within specification is shipped as product.[6]

3.4.2 GTSP from Limestone Treatment

GTSP is made from limestone in the reaction

$$2\ H_3PO_4 + CaCO_3 \rightarrow CaH_4(PO_4)_2 \cdot H_2O + CO_2$$

The product contains 45 to 50% available P_2O_5.[7]

Dilute, 22-38% P_2O_5 phosphoric acid and limestone are reacted in an agitated vessel system. Fines from the granulation circuit can be added, and reacted slurry can be recycled to disperse the reactants. The final slurry goes to a granulator, where pellets are formed and then dried and screened. The reaction appears complete in the liquid phase, and the resultant stable granulator product does not continue to emit fluorides.[7] The only fluoride entering this process is that contained in the WPPA fed.

3.5 PHOSPHATE ROCK DRYING AND GRINDING

Wet rock from mining and beneficiation contains from 7 to 20 percent moisture. Some customer contracts require 3 percent maximum moisture. Rock is dried to comply with that requirement. The two types of dryers used in the field are rotary and fluid bed dryers. The rotary dryers are inclined parallel flow units equipped with steel lifting flights, and are 2.1 or 2.4 meters (7 or 8 feet) in diameter. The fluid bed dryers operate by passing hot gases up through a perforated grating, which agitates and dries the rock. The dryers are primarily fired by oil, but use natural gas on standby service. The rock is discharged from the dryers at a temperature range of 100°C (212°F) to 140°C (284°F) onto conveyor belts feeding dry storage bins.[8]

Some phosphate rock is pulverized at the mines and shipped to the customer ready for acidulation. To accomplish this, the rock is conveyed to the grinder after it has been dried. There, it is ground, then conveyed to the storage bin or loaded directly into the car. Some phosphate rock is also pulverized for direct soil application, to a fineness of 85 percent less than 0.07 millimeter (0.003 inch) particle size. This rock is bulk-loaded into cars, or is conveyed to a machine where it is bagged, normally in 45-kilogram (100-pound) bags.[8]

Drying is often eliminated. Rock, containing 6 to 20% moisture, is transported from the beneficiation plant to the chemical plant where it is ground and chemically processed wet.[9,10]

3.6 PRODUCTION PROCESS CHANGES SINCE NSPS PUBLICATION

3.6.1 Production Processes in Use at Time of NSPS Publication

When the present NSPS was published in August 1975,[11] WPPA was made by dihydrate processes, SPA by submerged combustion or vacuum evaporation, DAP by the TVA and similar processes, run-of-pile TSP by phosphate rock treatment with phosphoric acid in the den process, and GTSP by treatment of run-of-pile TSP and by phosphate rock treatments with phosphoric acid that produce GTSP directly.[12]

3.6.2 Production Process Changes in the U.S.

In the U.S., there has been no substantial change in commercial production processes of WPPA, SPA, DAP, and run-of-pile TSP since NSPS publication.[13-30]

The production of GTSP by treating limestone with phosphoric acid is a new process introduced by the J.R. Simplot Co. at its Pocatello, Idaho plant.[31]

The elimination of phosphate rock drying by wet-rock grinding, prior to chemical processing is an important change of production practice. Wet-rock grinding facilities are in full-scale operation in phosphoric acid plants at the Plant City complex of C.F. Industries (Florida), at Agrico Chemical's Faustina (Louisiana) facility, and at both the old and new plants of W.R. Grace's Bartow complex (Florida).[9] IMC is also converting its dry-rock grinding operations to wet grinding at its New Wales phosphate chemicals complex (Florida).[32] Rock dryers and grinders are not affected facilities under this NSPS review study.

There have been no reports of commercial WPPA production by hemihydrate or hemidihydrate (HDH) processes in the United States; however, the Heyward-Robinson Company of New York is now marketing the hemihydrate process developed by Nisson Chemicals of Japan.[33] Occidental Research Corporation claims development of a proprietary method to make WPPA by the hemihydrate process.[34] Also, TVA has demonstrated pilot plant production of WPPA by its "hemihydrate foam" process.[35]

3.6.3 Production Process Changes Outside the U.S.

A commercial plant using the HDH process, developed by Fisons Ltd. in the United Kingdom (UK), is now producing WPPA in Trepca, Yugoslavia. The plant was designed and built by Lurgi Chemie and Huettentechnik GmbH of West Germany. A similar plant for Albright & Wilson at Whitehaven, UK, is under construction.[2] HDH plants are also in commercial use in Japan. The HDH process has been used commercially since 1974.[33,36]

3.6.4 Discussion of Limestone Treatment (Simplot) Process for GTSP Production

In the Simplot process, when H_3PO_4 in WPPA is reacted with $CaCO_3$ to make GTSP, fluorides are present only in the WPPA. Thus the only fluorides that might be emitted are the residual fluorides (H_2SiF_6 or HF and SiF_4) in the WPPA.

In the old GTSP process, when fluorapatite ($Ca(PO_4)_6F_2$) in phosphate rock is reacted with H_3PO_4, the fluorides present are comprised of both the fluorapatite fluoride content and the WPPA residual fluorides.

It follows from the above that the new Simplot process would emit much less fluoride (uncontrolled) than the old GTSP process, for each mole of monocalcium phosphate ($CaH_4(PO_4)_2 \cdot H_2O$) in GTSP produced. However, the phosphate content of each $CaH_4(PO_4)_2 \cdot 2H_2O$ molecule, produced in either process, is derived, ultimately, from fluorapatite. Therefore, the emittable fluorides from the total processing of fluorapatite to make one mole of $CaH_4(PO_4)_2 \cdot H_2O$ is the same regardless of whether the old process or the Simplot process is used. Potential fluoride emissions from the Simplot process are lower only in the absence of the WPPA plant.[37]

The Simplot process provides a means of reducing local fluoride emissions at the plant where it is applied. Fluorapatite is not used as a feed material, so this fluoride source is eliminated. Excess limestone can also be fed to precipitate the fluoride in the WPPA as insoluble calcium fluoride (CaF_2). In contrast, the old process emits more fluorides which require more scrubbing water and therefore larger pond areas. The amount and complexity of emission control equipment is reduced by the Simplot process. The company has found that the only gas cleaning

devices necessary are a scrubber on the dryer and conventional (uncoated) baghouses on other system components, e.g. screens and elevators.[38]

Results of the NSPS compliance test at the Simplot plant showed average emissions of 0.187 lb F (fluoride)/ton P_2O_5 fed.[31] The requirement for NSPS compliance in GTSP production is 0.20 lb F/ton P_2O_5 fed.

3.6.5 Discussion of Wet-Rock Grinding

Drying and grinding of phosphate rock can cause particulate emissions to the atmosphere. The particles can escape as dust if dryer gases are uncontrolled, as well as during grinding, especially if the materials are very dry. Dust can also be a significant problem at each point of transfer of the materials. The size of the dry, ground phosphate rock particle is less than 0.07 millimeter (0.003 inch).[39]

The world's primary phosphate occurrences are of sedimentary origin and contain radioactive materials, predominantly uranium and its decay products. Uranium, along with a very small amount of thorium, is thought to have been deposited contemporaneously with the phosphate. Phosphate rock in central Florida contains uranium concentrations of between 0.01 and 0.02 percent; despite the fact that uranium ore mined in the western United States solely for its uranium content contains 10 to 20 times this concentration, the phosphate industry currently mines slightly more total uranium than does the uranium industry.[40]

Under the Environmental Impact Statement for the Central Florida Phosphate Industry, proposed action will eliminate rock drying with certain exceptions where approved dryers will be used. This will decrease sulfur dioxide (SO_2) and dust emissions in Polk County caused by drying, grinding, and transportation as mines in that county are depleted and new mines are opened elsewhere. Since the new mines will ship wet rock, an estimated 1140 metric (1250 short) tons per year of dust and 7090 metric (7800 short) tons per year of SO_2 emissions from dryers in Polk County will not migrate into adjoining areas. The emissions from existing rock drying will decrease as the dryers are phased out.[41]

Reduction in radiation levels will occur as dry-rock grinding is replaced with wet-rock grinding and dryers are eliminated. This will lower fugitive dust levels, thus lowering escaping radionuclides, and also result in lower radiation levels in the immediate vicinity of the grinders and the eliminated dryers.[41]

Wet-rock grinding has four advantages:

(1) Reduces by about half the capital expense - from receipt of unground wet rock through the point of feeding it into the acid processing system.[42]

(2) Eliminates dry-rock dust pollution.[42]

(3) Improves fuel economy by 2.5 gallons per ton of phosphate rock ground, which combines with electrical power savings to reduce operating costs by \$3.00-\$4.25 per ton of P_2O_5.[42]

(4) Improves reliability, thus, reducing the required amount of surge of ground rock. If a plant is located near a mine, a rock slurry can be pumped directly to the plant from the mine, eliminating rail transportation and belt conveyors.[42]

By converting from dry to wet grinding, IMC expects to save 8 million gallons of fuel oil and 18 million kWh of electricity per year in producing WPPA at its New Wales complex. Conversion will cost about $11.3 million.[32]

3.6.6 Discussion of Hemihydrate (Hemidihydrate) Processes for WPPA Production

Solutions to three WPPA production problems are claimed for the two-stage HDH process: (1) energy consumption, (2) gypsum disposal, and (3) fluoride emission.[2]

Energy consumption is reduced by avoiding the need for evaporative concentration of product acid.[2]

The gypsum produced is reported to be of sufficient purity for use in building material.[2] Gypsum from conventional dihydrate processes cannot be so used because of its radioactivity level.

Fluoride emissions are controlled by recovery reported to be greater than 99% in a co-installed, on-line system. The recovered fluorides may be concentrated to 20 to 24% H_2SiF_6.[2]

Capital cost savings are reported for the HDH process (compared with the dihydrate process) in rock grinding, steam used for acid concentration, weak acid intermediate storage, and product acid clarification. These savings are partially offset by a larger reaction volume and filter area requirement. The capital cost for recrystallization and dihydrate filtration approximately equals that for acid concentration in dihydrate processes. An overall 5 to 10% capital cost reduction for the HDH process, compared with dihydrate processes, has been reported. Operating costs are also reported lower for the HDH process, mainly because of P_2O_5 recovery exceeding 98%, and low steam consumption.[2]

In the HDH process, recrystallization depends largely on phosphate rock composition. Morocco rock is used at the Trepco, Yugoslavia, plant. The planned Whitehaven, UK, plant is designed to use Morocco rock, but is reported capable of processing other rocks such as Florida rock.[2]

Reasons given for not using HDH processes in the U.S. include:

1. Uranium recovery is practiced by many plants in the U.S., and is reported to be greater from the more dilute phosphoric acid produced in dihydrate processes. About 1 lb uranium/ton P_2O_5 is recoverable. At about $40 per pound of uranium, it is more economical to use the current dihydrate process, recover the uranium, and finally concentrate the acid from 28 percent.[43]
2. Florida rock is not of sufficiently high quality to allow its use.[36]
3. Problems are encountered in the filtration operation when using Florida rock.[36]
4. The relatively large amount of clay fines and other impurities make this process difficult to control.[36]

3.7 STATUS OF POTENTIAL REGULATION OF RADIOACTIVE EMISSIONS FROM PHOSPHATE PLANTS UNDER THE CLEAN AIR ACT

The Office of Radiation Programs (ORP) of EPA has been assigned the responsibility for potential standards for radioactive emissions.[44] ORP has furnished the following information regarding the status of that work as it relates to phosphate plants.[45]

"Phosphate ore deposits contain radioactive materials primarily in the form of uranium-238 and its decay products. The concentrations of these radioactive materials in phosphate ores range up to 100 times greater than the concentrations of these materials in normal soils and rocks. Therefore, the mining and processing of phosphate ore has the potential for releasing quantities of radioactive materials into the atmosphere which may be of public health concern.

"The Environmental Protection Agency, as required by Section 122 of the Clean Air Act as amended in 1977, is presently reviewing available information to determine whether emissions of radioactive materials into the environment will cause or contribute to air pollution which may reasonably be anticipated to endanger public health. If the Agency makes a positive determination, then radioactive materials most probably will be listed as hazardous pollutants under Section 112 of the Clean Air Act and emission standards established for sources emitting important quantities of radioactive materials.

"Studies are now in progress to assess the health impact from emissions of radioactive materials from phosphate processing activities. These studies include development of information on the emission levels, pathways of human exposure and health risks to the exposed populations. The results of these studies will be evaluated to determine if a need exists to establish standards under Section 112 of the Clean Air Act for phosphate processing plants. Some preliminary results of these studies have already been published in the following EPA reports:

(1) "Radiation Dose Estimates Due to Air Particulates Emissions from Selected Phosphate Industry Operations," Technical Note, ORP/EERF-78-1, June 1978.

(2) Radiological Surveys of Idaho Phosphate Ore Processing - the Thermal Process Plant, Technical Note, ORP/LV-73-3, November 1977.

(3) Radiological Surveys of Idaho Phosphate Ore Processing - the Wet Process Plant - Technical Note, ORP/LV-78-1, April 1978."

3.8 REFERENCES FOR SECTION 3.

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18. Telecon. W. Herring to J. Symes, State of Florida. April 23, 1979. Subject: Phosphate Industry in Florida.

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4. FLUORIDE EMISSION CONTROL CHANGES

4.1 CONTROL SYSTEMS PREVIOUSLY AVAILABLE

Systems available to control fluoride emissions (hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4)), when the NSPS for phosphate plants was published in August 1975, consisted of scrubbers. Gypsum pond or cooling pond water was used as scrubbing media. Spent scrubbing water was returned to the plant pond system without chemical treatment. The spray-crossflow packed bed scrubber, shown in Figure 4-1, was generally used in the more effective scrubbing systems. A venturi scrubber was used in series with and before the spray-crossflow packed bed unit for gas streams having high solids content, and where solids might precipitate from scrubbing solution, as in granulated triple superphosphate (GTSP) and diammonium phosphate (DAP) processes.[1]

The spray-crossflow packed bed scrubber consists of two sections - a spray chamber and a packed bed - separated by a series of irrigated baffles. Both the spray and the packed sections are equipped with a gas inlet. Effluent streams with relatively high fluoride concentrations - particularly those rich in SiF_4 - are treated in the spray chamber before entering the packing. This preliminary scrubbing removes SiF_4 thereby reducing the danger of plugging the bed. At the same time, it reduces the loading on the packed stage and provides some solids handling capacity. Gases low in SiF_4 can be introduced directly to the packed section.[1]

The spray section accounts for approximately 40 to 50 percent of the total length of the scrubber. It consists of a series of counter-current spray manifolds with each pair of spray manifolds followed by a system of irrigated baffles. The irrigated baffles remove precipitated silica and prevent the formation of scale in the spray chamber.

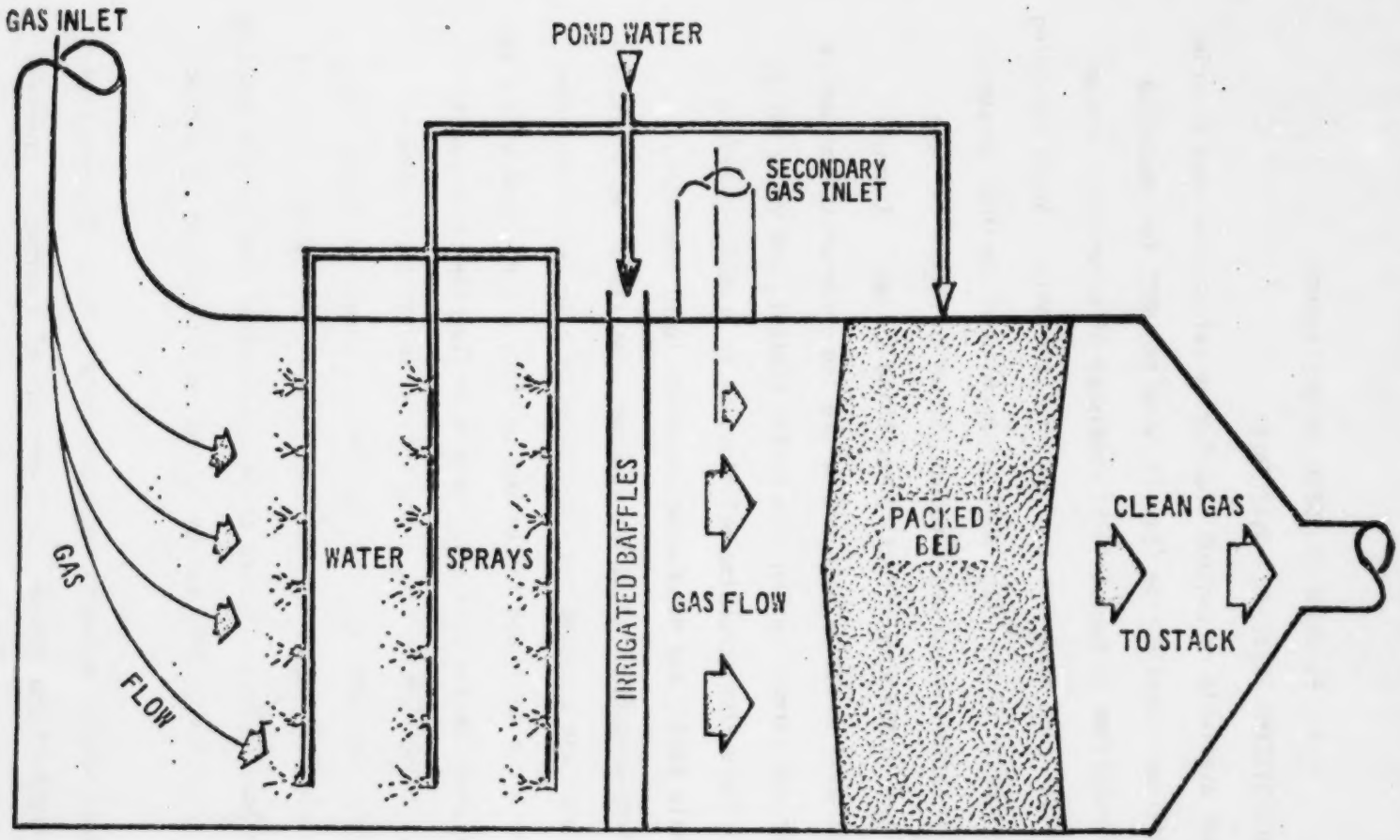

FIGURE 4-1. SPRAY-CROSSFLOW PACKED BED SCRUBBER.

In spray-crossflow packed bed scrubbers the gas stream moves horizontally through the bed while the scrubbing liquid flows vertically through the packing. Solids tend to deposit near the front of the bed where they can be washed off by a cleaning spray. This design also allows the use of a higher irrigation rate at the front of the bed to aid in solids removal. The back portion of the bed is usually operated dry to provide mist elimination.[1]

Pressure loss through the scrubber is usually 4 to 6 inches of water. Filters in the water lines ahead of the spray nozzles prevent plugging by suspended solids. The ratio of scrubbing liquid to gas ranges from 0.02 to 0.07 gpm/acfm depending upon the fluoride content - especially the SiF_4 content - of the gas stream. Approximately one-third of this water is used in the spray section while the remaining two-thirds is used in the packing.[1]

The packed bed is designed for a scrubbing liquid inlet pressure of about 4 or 5 pounds per square inch (gauge). Water at this pressure is available from the pond water recycle system. The spray section requires an inlet pressure of 20 to 30 pounds per square inch (gauge). This normally requires the use of a booster pump. Spent scrubbing water is collected in a sump at the bottom of the scrubber and pumped to a pond.[1]

4.2 NEW CONTROL SYSTEMS

Since NSPS publication, scrubbers have remained the principal means of controlling fluoride emissions from phosphate plants.[2-14] A few alterations of scrubbing system design have been introduced. These involve scrubbing to recover fluorides as saleable fluosilisic acid (H_2SiF_6) byproduct, and removing the remaining fluorides from the gas

by scrubbing with water that is cooled in closed-loop, cooling tower systems.[14-19] In some of these systems, scrubbing water is caustic treated, and a slip stream is limed to precipitate the fluoride as CaF_2 and regenerate the caustic.[14-18]

One phosphate production process variation has been introduced since NSPS publication, as a means of controlling fluoride emissions. That variation consists of making GTSP by treating limestone, instead of phosphate rock, with wet process phosphoric acid (WPPA). This process and its emissions were described in Section 3. PRODUCTION PROCESS CHANGES.

A revised process for phosphate rock processing has been introduced. Emissions, including radioactive constituents, evolved during rock drying and grinding, are reduced by eliminating drying and by grinding the rock wet. This process was also described in Section 3.

4.2.1 Revised Scrubbing Systems for WPPA and TSP Production

A revised scrubbing system is used at one plant complex in Mississippi to control fluoride emissions from WPPA and triple superphosphate (TSP) production.[15]

In the WPPA process at this plant complex, gases from the phosphate rock acidulation reactor are treated in a spray-crossflow packed bed scrubber to collect fluorides. Water from gypsum pond overflow is used as the scrubbing medium. Gases from the reactor vacuum cooler and from four vacuum evaporators used for acid concentration go to a series of low-pressure-drop cascade scrubbers. Each cascade scrubber receives gas from one vacuum cooler or evaporator. The scrubbing water from the reactor scrubber is used in the cascade scrubbers, removing additional

fluoride from the gases in each, finally leaving the scrubber train as byproduct 23% H_2SiF_6. To avoid deposition of gelatinous $Si(OH)_4$, which might plug equipment, the arrangement of gas and liquid streams flowing to each cascade scrubber must be in an order that effects a satisfactory F/Si ratio in the scrubbing liquid. This system is reported to recover 99% of the gaseous fluorides emitted during acidulation and acid concentration as saleable H_2SiF_6.[14-18]

Gases from each cascade scrubber go to one of the series of plant barometric condensers where the remaining fluorides are collected. The water from the barometric condensers, at pH 3-3.5 and 120°F, goes to a cooling tower where sodium hydroxide (NaOH) is added to the stream to increase its pH to greater than 4, reduce fluoride vapor pressure, and prevent fluoride emissions from the tower. Make-up water is also added. The resulting liquid stream leaves the cooling tower at 90°F, then returns to the barometric condensers, forming a closed loop. A slip stream from the cooling tower is treated with calcium hydroxide ($Ca(OH)_2$) to obtain pH 11.5-12 and precipitate the fluorides in a crystalline product composed of fluoride and silicate salts of calcium. This product is presently landfilled but has potential use as glass raw material.[14-18]

Fluorides emitted from TSP production and storage facilities at the above plant complex are also collected in scrubbers. The TSP scrubbing system is incorporated as a portion of the WPPA closed-loop cooling tower system.[20] Quantities of fluoride emissions from TSP production are smaller than those from WPPA production; and emissions from production of both products can be handled compatably since they are derived from the same basic raw materials and therefore, consist of similar constituents.

In addition to the use of cooling towers with caustic treatment of water, as just described, cooling towers are used or planned for use at several other phosphate plants in closed-loop water handling systems, but without any reported water treatment to reduce fluoride vapor pressure. In some of these systems, process gas is treated in Swift spray-chamber scrubbers to recover fluoride as byproduct H_2SiF_6.[19] In the usual plant arrangement, the Swift scrubbers are positioned between the acid-concentration vacuum evaporators and the barometric condensers, and provide 65 to 90% fluoride recovery.[18,19] In at least one plant, the process gas is not treated to recover fluorides prior to final scrubbing; and the resulting scrubbing water is cooled in a closed-loop cooling tower without caustic treatment.[21]

4.2.2 Revised Scrubbing System for DAP Production

A revised scrubbing system is used to control fluoride emissions from DAP production at three NPK (nitrogen, phosphorous, potassium mixed fertilizer) plants at the previously mentioned Mississippi plant complex.[15] Gases from the preneutralizer and granulator first go to a venturi scrubber where most of the ammonia (NH_3) in the gas is absorbed in dilute phosphoric acid. Residual ammonia leaves the venturi, in the outlet gas, as gaseous NH_3 or as submicron particulate ammonium fluoride (NH_4F) or ammonium bifluoride ($NH_4F{\cdot}HF$). Phosphoric acid might be contained in the venturi outlet gas in entrained liquid particles.[15-18]

The gas from the venturi goes to the first stage (nitrogen-phosphorous removal section) of a two-stage spray-crossflow packed bed scrubber where residual ammonia and phosphates are removed in additional dilute phosphoric acid scrubbing liquid.[16,17]

The scrubbing solution leaving the venturi and the spray-crossflow packed bed first stage goes to the sump of the venturi scrubber. It is treated with make-up dilute phosphoric acid and then recycled to both the venturi and the spray-crossflow packed bed first-stage scrubbers. Another stream from the venturi sump returns part of the solution to the DAP process in the preneutralizer feed stream, to recover the NH_3 and phosphates.[16,17]

The remaining fluorides in the exit gas from the spray-crossflow packed bed scrubber first stage are removed in the second stage of that scrubber. The scrubbing water for the second stage is cooled in a cooling tower and treated with NaOH in a closed-loop system to increase its pH and limit fluoride emissions from the tower. A slip stream of water from the tower is limed to precipitate the fluoride and regenerate the NaOH.[15,16,17]

Gases from the DAP dryer are treated in a scrubbing system similar to that just described for the DAP preneutralizer and granulator gases. Gases from the cooler may also be similarly treated or might be sent to the inlet of the spray-crossflow packed bed scrubber treating the DAP dryer gas, thus being treated as a part of that gas stream.[16]

The system for handling gas from DAP production, including the cooling tower, is segregated from that used for WPPA and TSP process gases to keep nitrogen compounds out of the WPPA-TSP system.[20]

4.2.3 Discussion of Revised Scrubbing Systems

By employing NaOH to increase the pH of scrubbing solution and reduce fluoride vapor pressure, scrubbing systems can provide for a potential fluoride emission reduction estimated as much as 75% below present achievement levels.[18] Maintenance problems, however, are reported

to restrict scrubbing efficiency. Applicable standards are met when packed beds are in good order, but maintaining that condition is reported to be difficult.[20]

A plant representative states that the system has not yet been perfected. Refinements are still being made, and more time is needed to develop improved utilization of the system. Packed beds become clogged. Various types of packing and washing techniques are being tried to overcome clogging. Deterioration of rubber scrubber lining has necessitated relining in less than one year of usage. Some lined components have had to be replaced with stainless steel. Maintaining service is generally difficult because of corrosion of steel parts.[20]

The closed-loop scrubbing system, employing cooling towers and alkali water treatment, was installed mainly to improve water utilization and prevent water pollution. This purpose has been met satisfactorily. Because of high rainfall in its Mississippi location, the plant complex cannot use all of the water that falls on its property. The plant gypsum pond system collects the rain water, and pond overflow feeds all plant processes. Any excess water must be treated before release.[20] The plant land area is too limited to provide for cooling ponds of sufficient size to accept the cooling duty for the WPPA and TSP processes.[14] The closed-loop system avoids the unacceptable alternative of taking water into the plant from the nearby bayou, using it for scrubbing, then returning it to the bayou.[20] It also reduces the total amount of plant water that must be treated before leaving the plant.

By eliminating the cooling pond, the closed-loop scrubbing system with alkali treatment is estimated to reduce plant pond area and fluoride emissions from the ponds by at least 50%.[14,17,18]

Phosphate plants converting from cooling ponds to cooling towers are located in Louisiana.[19] As in the Mississippi plant complex just discussed, rain added to water from plant processes causes water levels in ponds to increase. Therefore, water must be recycled for disposal.[13] Cooling towers effect evaporative cooling, while pond cooling is largely by convection.[19] Thus, cooling towers appear advantageous for reducing quantities of water that must be handled in recycling and disposal. They seem, therefore, to be coming into increased use in states with high rainfall.

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6. Telecon. W. Herring to G. McNeill, U.S. EPA Region 4. April 18, 1979. Subject: Phosphate Industry in Region 4.

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10. Telecon. W. Herring to R. Stenner, State of Idaho. April 19, 1979. Subject: Phosphate Industry in Idaho.

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12. Telecon. G. Wallin, State of Texas, to W. Herring. April 30, 1979. Subject: Phosphate Industry in Texas.

13. Telecon. W. Herring to O. Tanner, State of Louisiana. May 1, 1979. Subject: Phosphate Industry in Louisiana.

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18. Teller, A.J. Scrubbers in the Fertilizer Industry, Their Success, Near Future, And Eventual Replacement. (Meeting, Fertilizer Round Table. Washington. Nov. 1973.) pp. 150-158.

19. Telecon. J. Dehn, EPA Region 6, to W. Herring. April 27, 1979. Subject: Phosphate Industry in Region 6.

20. Telecon. W. Herring to A. Gentry, Mississippi Chemicals Co., May 16, 1979. Subject: Emission Control at Pascagoula Plant.

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5. ADVANCES IN GYPSUM POND FLUORIDE CONTROL

5.1 PREVIOUS OPERATION AND CONSTRUCTION OF POND SYSTEMS

When the phosphate industry NSPS was published in August 1975, liquids entering gypsum ponds at plants in the U.S. consisted principally of rainfall plus the process streams listed below. These process streams were formed from recycled gypsum pond water plus fluorides and other substances generated in the processes.[1]

5.1.1. Discharge streams from dihydrate processes making wet process phosphoric acid (WPPA).

1. Gypsum slurry (filter cake slurried with pond water). Approximately 2.5 pounds of gypsum are produced per pound of pure phosphoric acid[2], or 1.2 pounds of gypsum per pound of 30% phosphoric acid.[3]

2. Liquid from barometric condensers that treat gas from (a) the reactor vacuum cooler, and (b) the vacuum evaporators that concentrate the WPPA. At some plants, the gas from the WPPA evaporators might have been treated in scrubbers for flousilisic acid (H_2SiF_6) recovery prior to entering the barometric condensers.

3. Liquid discharged from the scrubber that treats gases from the acidulation reactor, filters, hot wells, and filtrate seal tanks.

5.1.2 Superphosphoric acid (SPA) process discharge streams.

1. Liquid from the barometric condenser that treats gas from the vacuum evaporator.

2. Liquid from heat-exchanger cooling tank.

5.1.3 Diammonium phosphate (DAP) process discharge streams.

1. Liquid from the scrubbers that treat gases from the reactor, granulator, dryer, and cooler.

5.1.4 Run-of-pile (ROP) triple superphosphate (TSP) process discharge streams.

1. Liquid discharged from the scrubbers that treat gases from the mixer, den, and storage building.

5.1.5 Granular triple superphosphate (GTSP) process discharge streams.

1. Liquid discharged from the scrubbers that treat gas from the reactor, granulator, dryer, cooler, and screens.

Gypsum ponds are generally dyked areas.[4] In the past, they have usually not been lined to prevent seepage.[3] The gypsum pond serves two purposes: (1) as a settling and storage area for waste gypsum, and (2) as an area for cooling process water prior to reuse.[2]

Figure 5-1 is a simplified representation of a typical gypsum pond serving a 1000-ton/day-P_2O_5 WPPA plant. This pond, handling both slurry and process water, would have about 350 acres of wet area. Water depth would be about 10 feet. Most likely it would be located adjacent to the plant and surrounded by mined-out land of sparse vegetation or swamp. Assuming that the pond is used for both gypsum settling and cooling, there is a region where the stream from the sluicing operation joins the pond. This area, known as the gypsum flats, is where the gypsum settles. It is constantly worked by draglines, which remove settled wet gypsum and transfer it onto an active gypsum pile

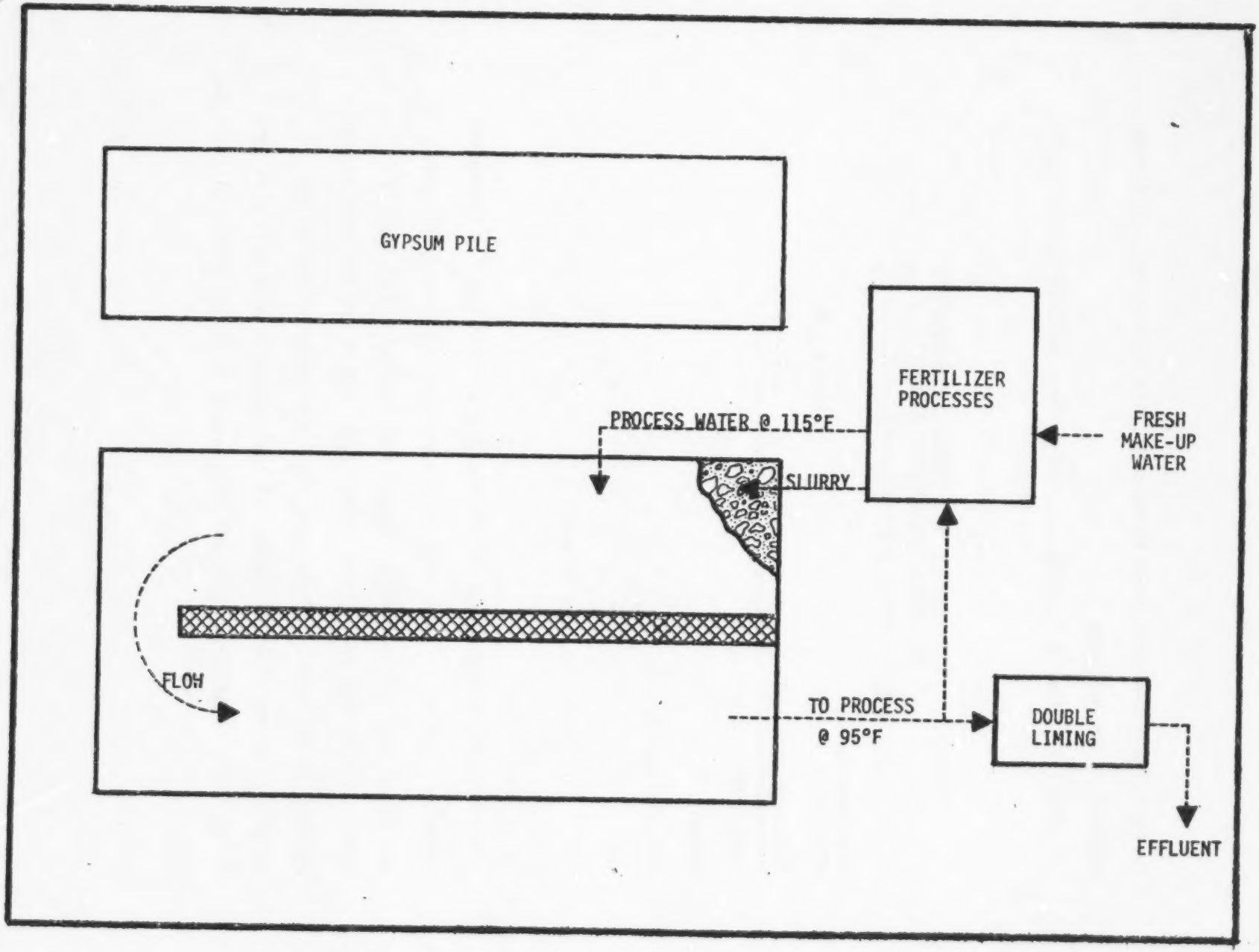

Figure 5-1. Typical gypsum pond servicing a 1000-ton/day P_2O_5 plant.

to dry. The gypsum pile would be about 80 feet high on about 150 acres adjacent to the wet pond.[5]

Table 5-1 shows a fluoride material balance for WPPA production.[6]

TABLE 5-1

TYPICAL MATERIAL BALANCE OF FLUORIDE IN MANUFACTURE OF WET-PROCESS PHOSPHORIC ACID

BASIS: 100 LB PHOSPHATE ROCK

Fluoride-bearing material or source	Fluoride, lb
Phosphate rock	3.9
Product wet process acid	1.0
Gypsum	1.2
Barometric condensers	1.67
Air	0.03
Total fluoride output	3.9

Fluorides in the gypsum slurry and in the water from the barometric condensers and the scrubber that treats process emissions to air go to the gypsum pond. It therefore follows from Table 5-1 that over 70 percent of the fluorine content of the rock used in the wet-acid process may pass to that pond. If the same plant also produces DAP or TSP, a large part of the fluorine content of the phosphoric acid will also pass to the gypsum pond through the water scrubbers in these additional processes.

Thus, 85 percent or more of the fluorine originally present in the phosphate rock may find its way to the gypsum pond. Fluoride associated with the gypsum is, however, in insoluble form, probably as calcium fluoride (CaF_2), before being sent to the pond.[6,7] It is believed that fluorides from the barometric condensers are the primary source of pond emissions.[8]

In gypsum ponds, approximately one acre foot of disposal volume is required per year for each daily ton of P_2O_5 produced by the plant.[4] Based on wet process phosphoric acid production, plants have gypsum ponds of surface areas in the range of 0.1-0.4 acre per daily ton of P_2O_5. Thus a large plant may have a gypsum pond with a surface area of 200 acres or more.[9]

The water of pond systems is normally acid, having a pH around 1.5. This acidity is probably due mainly to inclusion of phosphoric acid in the washed gypsum from the gypsum filter.[10]

Gypsum pond water can be expected to contain from 0.2 to 1.5 percent fluosilicic acid (2000-12,500 ppm F) or most often, 5000-6000 ppm F. The fluosilicic acid decomposes to silicon tetrafluoride and hydrogen fluoride, resulting in a vapor-liquid equilibrium. The fluoride concentration of a given pond does not continue rising as fluorides are added, but tends to stabilize. This action may be due to precipitation of complex calcium silicofluorides in the pond water.[10]

Published emission factors from gypsum ponds range from 0.2 to 10 lb F/acre-day. Table 5-2 shows the emission factors obtained from one comprehensive investigation.[11]

Table 5-2 FLUORIDE EMISSION FACTORS FOR SELECTED GYPSUM PONDS AT 90°F (lb/acre-day)

	Wind velocity at 16 ft elevation, m/sec			
	1	2	4	6
Pond 10 (6,400 ppm F)	0.8	1.3	2.3	-
Pond 20 (12,000 ppm F)	0.8	1.3	2.3	3.2

The most recent measurements of fluoride emissions from gypsum ponds indicated fluoride concentration above the pond of 18 to 46 parts per billion (ppb), consisting almost entirely of hydrogen fluoride (HF), as measured by the Remote Optical Sensing of Emissions (ROSE) system. Emission rates of 0.2 to 7.3 lb F/acre-day were indicated by concurrent wet sampling and analysis.[12]

Gypsum ponds also contain radioactive material.[13] Dried areas of ponds are a possible source of radioactive emissions to the atmosphere.[14] Radioactive emissions from phosphate plants are being investigated by the Office of Radiation Programs, EPA, for possible regulation.[15] The status of this investigation is reported in Section 3, "PRODUCTION PROCESS CHANGES."

5.2 PRESENT OPERATION AND CONSTRUCTION OF POND SYSTEMS

Since NSPS publication, information on ponds not previously reported, including a few changes in gypsum pond operation and construction, has been published. This information is shown below. Apart from the changes noted, present pond operation and construction is the same as described above.

5.2.1 Treatment of Pond Water for Discharge

When rainfall exceeds evaporation, water is discharged from the pond. This water has been treated prior to entering a natural water course.[5] Successful treatment of discharges has been demonstrated by the use of a two-stage process; in the first stage the discharge passes through limestone (calcium carbonate), which effectively increases the pH to approximately 4.5 and in the second stage hydrated lime in used to increase the pH to more than 7. This process reduces fluoride to less than 10 milligrams per liter, phosphate to approximately 30 milligrams per liter and radium to less than 1 picocurie per liter.[3]

5.2.2 Pond Lining

The Environmental Impact Statement (EIS) for the Central Florida Phosphate Industry includes the proposed requirement:

"Line gypsum ponds with an impervious material unless it can be demonstrated in the site-specific EIS that such lining is unnecessary in protecting ground water from chemical and radiological contamination."[16]

Since Florida plants account for most WPPA production capacity in the U.S., and would, therefore, have the majority of gypsum ponds,[4] most new ponds constructed in the U.S. will probably have impervious linings.

5.2.3 Pond Area Reduction by Cooling Towers and Fluoride Recovery

Phosphoric acid plants utilize a wide variety of gypsum cooling pond arrangements. In most cases process and gypsum sluicing waters are transported to a common pond allowing these waters - which are vastly different in properties - to mix, with the ultimate result that both process and gypsum pond waters become highly contaminated with phosphoric acid, H_2SO_4, and H_2SiF_6.[17]

In some cases, separate cooling and gypsum ponds are utilized. All process waters except gypsum sluicing water are sent to cooling ponds. Gypsum slurry is pumped from the filtration operation to a gypsum pile where the gypsum settles. The supernatant water is subsequently recycled through the cooling pond, thus contaminating it with phosphoric acid, H_2SO_4, and fluorides from the filtered gypsum.[17]

The required size of the gypsum slurry pond is small (about 5 acres) since no area is required for cooling. This water would be the most contaminated and acidic water in the plant because of the presence of phosphoric acid, H_2SO_4, iron and aluminum complexes, and fluorides from the filtration operation.[17]

The pond area required for the barometric condensers is determined by the cooling duty requirements. This area is estimated to be 0.1 acre per ton of P_2O_5 per day.[17]

Since the cooling pond receives condensed vapors from the flash cooler and evaporators, entrained phosphoric acid could be present as a contaminant. This, however, can be minimized by entrainment separators so that the main contaminant entering the cooling pond could be limited to fluorides.[17]

Since NSPS publication, cooling towers have been introduced, in place of cooling pond area, at phosphate plants as described in Section 4, "FLUORIDE EMISSION CONTROL CHANGES." In these applications, fluorides in the gases from the WPPA vacuum cooler and vacuum evaporators are scrubbed to recover the fluorides as H_2SiF_6 prior to final scrubbing in the process barometric condensers. Water from the WPPA-reactor scrubber is used to scrub the vacuum cooler/evaporator gases, thus effecting further fluoride recovery. Recovery efficiencies as high as 99% are reported. The water from the barometric condensers is cooled in closed-loop cooling tower systems. In some of these systems, the scrubbing water in the closed loop is caustic treated and a slip stream is limed to precipitate the fluorides for disposal, and to regenerate the caustic. With cooling pond area thus mostly eliminated, pond systems are reduced to the principal function of handling gypsum slurry.[18]

From Table 5-1, most of the soluble (potentially emittable) fluorides are contained in the gases routed to the barometric condensers. Additional fluorides are contained in the gases from the WPPA reactor. Since the fluorides from both of these sources are efficiently recovered and converted to the saleable H_2SiF_6 byproduct, and since pond area is reduced by removal of pond thermal load by cooling towers, pond area and pond fluoride emissions can be reduced at least one-half.[18]

5.2.4 Gypsum Pond Emission Reduction by Fluoride Recovery from WPPA Evaporator Gas

Fluoride emissions from the pond system at the W.R. Grace WPPA plant are reduced by the process described in the following excerpt from a letter to the EPA:

"The fluoride recovery system in the W.R. Grace phosphoric acid plant is the Swift & Co. process licensed to Grace by Swift. Fluorides are recovered in the form of hydrofluosilicic acid (H_2SiF_6) of approximate 25 percent strength. The process recovers approximately 65 percent of the fluorine in these vapors as 25 percent hydrofluosilicic acid, which calculates to approximately 25 percent fluorine recovery from the total coming in with the phosphate rock. The vapors leaving the phosphoric acid vacuum evaporators are scrubbed under vacuum with a recirculating solution of hydrofluosilicic acid whose temperature is approximately that of the vapors. Little or no water is condensed while the SiF_4 and HF are absorbed in the fluosilicic acid solution. The lean vapors from the fluorine scrubber are then passed to the usual barometric condenser for total condensation. A specific gravity controller activates a valve which discharges the H_2SiF_6 to storage when up to the desired strength. Makeup water then flows into the hot well through a float control valve."[13]

Pertaining to fluoride recovery as a means of reducing pond emissions, the Central Florida EIS includes the proposed requirement:

"Provide for recovery of fluorine compounds from phosphoric-acid evaporators unless it is determined at the time of permit application that market conditions are such that the cost of operation (not including amortization of initial capital cost) of the recovery process exceeds the market value of the product. If there is an exception, the site-specific EIS is to contain an estimate of pond-water fluoride concentrations to be attained and levels of

fluorine emission. Estimated fluorine emissions from new-source gyp ponds should not cause the plant complex to exceed the total allowable point-source fluorine emissions within the plant complex if a permit is to be issued."[16]

Also, from the Central Florida EIS, "Reported costs of fluoride recovery operations exceed prices by 25 to 36 percent. Fluoride is marketed for the fluoridation of water supplies and for use as an industrial chemical."[13]

5.2.5 Gypsum Pond Emission Reduction by Fluoride Recovery from WPPA Process Water

Fluoride emissions from the pond system at the USS Agri-Chemicals WPPA plant are reduced by the process described in the following excerpt from a letter to the EPA:

"As a result of development engineering in the late 1960s to generate a means of diluting concentrated sulfuric acid with wet-process phosphoric acid pond water and thereby eliminate production problems with respect to conventional sulfuric acid dilution coolers and simultaneously create a negative water balance in the phosphoric acid pond water system, an offshoot of this work was devised and a process resulted which would recover fluosilicic acid (FSA) from phosphoric acid.

"Our (USS Agri-Chemicals) process uses 22 percent of P_2O_5 recycle phosphoric acid from the filtration wash steps as a diluent for diluting 98 percent sulfuric acid. The heat of dilution drives off silica (sic) tetrafluoride (SiF_4) from the 22 percent recycle stream, along with water vapor. The hydration product is a 25

percent H_2SiF_6 fluosilicic acid of extremely low P_2O_5 content. Conventional processes for stripping FSA during phosphoric acid evaporation produce FSA containing between 0.5 and 2 percent P_2O_5. Our process consistently produces FSA with a content well below 0.3 and frequently under 0.1 percent P_2O_5 (100 percent H_2SiF_6 basis).

"We installed a commercial unit which became operational in May 1970 as a first of its kind at a total capital cost of $1.5MM. In addition to reclaiming FSA through the recycle acid dilution route, we built certain flexibilities in the commercial plant to innovate recovery of FSA from fluorine scrubber systems from the triple super phosphate (TSP) manufacture and from steam stripping of the final concentrated phosphoric acid. The latter two process adjuncts did not prove satisfactory and have since been abandoned. I cannot project accurately the capital costs of a unit designed and built for recycle acid service only on today's cost basis but would guess at least $2.5MM.

"Since this was an entirely new concept and the process conditions were extremely severe, the operating costs and profit benefits have been considerable less than satisfactory. Mechanical and corrosion problems resulting from the stringent operating conditions have led to prohibitive maintenance costs. The process deals with high-temperature mixes of sulfuric acid and phosphoric acid in an atmosphere of fluoride compounds, all of which contain abrasive, precipitated SiO_2 and calcium sulphate (gypsum). The high temperatures tend to promote the anhydride formation of calcium sulphate, and scaling is

a serious problem. We have learned to live with the process and, though it now performs well, it is a costly operation."[19]

5.2.6 Gypsum Pond Reduction by Hemihydrate WPPA Production

As discussed in Section 3, "PRODUCTION PROCESS CHANGES", gypsum produced in the hemihydrate (hemidihydrate or HDH) process for WPPA is reported suitable as building material. Sale of this material would greatly reduce its accumulation in the gypsum pile and in ponds.[20]

The HDH process has not, however, been commercially demonstrated in the U.S.; commercial plants in Europe and Japan have been reported.[20]

5.3 REFERENCES FOR SECTION 5.

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2. Linero, A.A. and R.A. Baker. Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry. U.S. EPA. Washington, D.C. Publication No. EPA-600/2-78-124. June 1978. p. 3.

3. Central Florida Phosphate Industry Areawide Impact Assessment Program, Vol. 1: Description of Program and Industry. U.S. EPA Region 4. Atlanta, GA. Project No. 08-01-4196. Sept. 1978. p. 37.

4. Reference 2. pp. 6-7.

5. Reference 2. pp. 143-6.

6. Reference 1. pp. 5-6, 5-15.

7. Reference 2. p. 184.

8. Reference 2. p. 159.

9. Reference 1. p. 5-16.

10. Reference 1. p. 5-15.

11. Reference 1. pp. 5-16, 5-17.

12. Boscak, V.G., N.E. Browne, and N. Ostojic. Measurement of Fluoride Emissions from Gypsum Ponds, Draft Final Report. U.S. E.P.A. Washington, D.C. Contract 69-01-4145, Task 10. Sept. 1978.

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15. Memo from P.J. Magno, EPA (ORP) to G.B. Crane, EPA (OAQPS). June 20, 1979. Subject: Regulation of Radioactive Emissions from Phosphate Plants.

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17. Reference 2. pp. 154-5.

18. Telecon. G.B. Crane and W. Herring to A.J. Teller, Teller Environmental Systems, Inc., May 14, 1979. Subject: Review of Phosphate Fertilizer NSPS.

19. Reference 13. p. 2.24.

20. Blumrich, W.E., H.J. Koening, and E.W. Schwehr. The Fisons HDH Phosphoric Acid Process. Chemical Engineering Progress. 74: 58-61. Nov. 1978.

6. NSPS ENFORCEMENT PROBLEMS AND COMPLAINTS

6.1 EMERGING TECHNOLOGY SINCE NSPS PUBLICATION

Based on inquiries to EPA Regions 4, 5, 6, and 10, and the States of Florida, North Carolina, Illinois, Texas, Louisiana, and Idaho, source test data was obtained from only one phosphate production plant that was identified as an emerging technology.[1-18] That source is the J.R. Simplot Co. plant at Pocatello, Idaho, that makes granular triple superphosphate (GTSP). That plant began production of GTSP in March 1977, using a process variant that consists of treating limestone with wet process phosphoric acid (WPPA).[19-21] This process variant is described in Section 3, "PRODUCTION PROCESS CHANGES."

Results of the NSPS compliance test at the Simplot plant, submitted to the EPA Regional Administrator on Dec. 30, 1977, show average fluoride emissions of 1.11 lb/hr, or 0.187 lb/ton P_2O_5.[21] The requirement for NSPS compliance in GTSP production is 0.20 lb F (fluoride)/ton P_2O_5.

According to a State of Idaho estimate, the above emission rate compares with fluoride emissions from the old process as great as 43 lb/hr. The State also notes that the old process utilized the ROP/GTSP method where run-of-pile triple superphosphate (ROP) was manufactured and cured, and then GTSP was made from the cured ROP. The State notes further that the new process eliminates the ROP step and the new GTSP product thus goes to storage in the final cured state. High fugitive emissions are therefore eliminated in the storage area.[19]

6.2 COMPLAINTS OF PHOSPHATE PLANT EMISSIONS AND SUGGESTED IMPROVEMENTS OF REGULATIONS

Inquiries about complaints were made to representatives of EPA Regions 4, 5, 6, and 10, the states of Florida and North Carolina in Region 4, Illinois in Region 5, Texas and Louisiana in Region 6, and Idaho in Region 10. Responses indicated that public complaints applying to emissions from phosphate production facilities were limited to those summarized below.[1-18]

6.2.1 Florida

Region 4 has had recent complaints about phosphate plants in central Florida:

1. Heavy emissions are alleged to occur at night. The complaints indicate that control equipment is not maintained satisfactorily and not operated continuously.[1]

2. Excursions above allowable limitations of Florida regulations are alleged to affect blooms on orange trees.[1]

3. Plant neighbors report heavy fugitive emissions from GTSP storage facilities. These emissions have not occurred during Region 4 visits, but Region 4 representatives have seen pictures of them.[1,22]

The complaints on the central Florida plants were received from a total of five individuals during 1974 to 1979. They included five complaints from one individual in 1977.[22]

A Region 4 representative commented that there is currently no way of checking whether or when control equipment has been on or off. He suggested that NSPS should include continuous monitoring of controls

to show when equipment has been in service and operated per design specifications, and when not in service.[1]

The following public comments recorded in Volume III of the Environmental Impact Statement (EIS) for the Central Florida Phosphate Industry also appear pertinent:

1. "With respect to fluoride and uranium, recovery of these two compounds, based solely on economic consideration . . . is totally unacceptable in view of the documented damage caused by these compounds.

"They should be removed from the waste water as a simple matter of health protection. If a profit results, so much the better for the industry. But placing such an emphasis on profit is neither justifiable nor desirable from the public or environmental health standpoint."[23]

2. "We suggest you include the information that Florida has the highest rate of lung cancer in the United States, the statistics weighted so incidences are not attributable to age.

"It does not seem unreasonable to assume, based on studies by Goffman and others, that these lung cancers are related to the high levels of radioactivity in our region. Additionally, statistics readily available from the Department of HRS for last year show that Florida led the nation in deaths from cancer."[24]

3. "Without adequate, proper and timely monitoring by the federal and state environmental agencies, all proposed actions and existing rules, regulations and requirements are worthless and ineffective.

"Therefore, we request that adequate surveillance programs be instigated with an appropriate funding level in order to accomplish those goals which should be of the highest priority."[25]

Pertaining to the above comments on uranium and radioactivity, radioactive emissions from phosphate plants are being investigated by the Office of Radiation Programs, EPA, for possible regulation. The status of this investigation is reported in Section 3, "PRODUCTION PROCESS CHANGES."

6.2.2 Idaho

A State of Idaho representative stated that farmers have complained about contamination of cattle feed by fluoride emissions from the Simplot plant, mentioned above. He also said that private legal action against the company was taken by the farmers, and that the company has since reduced the emissions. Since the aforementioned legal action was taken privately, the State was not involved, and has not retained a file on this matter. The representative of the State commented, however, that it is too soon to know whether the emission reduction has been sufficient to stop harm to the cattle.[18,19]

6.3 STATUS OF DEVELOPMENT OF FLUORIDE MONITORING

Pertaining to the Region 4 suggestion that emission control systems be monitored, information was obtained on the current status of systems for monitoring fluoride emissions.

A continuous monitor for fluoride emissions was recently evaluated by the EPA Environmental Sciences Research Laboratory, which furnished the following comment:

> The monitor is designed to detect HF gas. Fluoride particulate is not included in the measurement. Should any particulate get

into the analyzer past the particulate thimble filter, the water-soluble portion of the particulate fluoride will be included in the selective ion electrode measurement.[27]

Pertaining to the same investigation, the EPA Emission Measurement Branch commented:

> These instruments have been around since initial promulgation [of the phosphate plant NSPS] and have not proven to be adequate for continuously monitoring total fluoride emissions. The instrument is designed to measure only gaseous fluoride and in field applications, has proven to be unreliable and produce erratic results. John Nader's report also points out these problems.[28]

6.4 STATE PLANS FOR REGULATING EXISTING PHOSPHATE PLANTS

The status of state plans for controlling fluoride emissions from existing phosphate plants, as of October 1979, under Section 111(d) of the Clean Air Act, is summarized as follows:

A. EPA Region 4

1. Negative declarations (no phosphate plants in state) were received from Alabama, Kentucky, Tennessee, South Carolina, and Georgia.[29]

2. North Carolina. Plan not yet submitted. State has one phosphate plant. State held a public hearing June 1978, and intends to submit 111(d) plan about December 1979. Requirements of plan are expected to be less stringent than 111(d) guidelines regarding granulated triple superphosphate (GTSP) storage. [29]

3. Mississippi. Plan not yet submitted. State has one phosphate plant. State requested extension to July 1979. [29]

4. Florida. Plan has been submitted. It is less stringent than 111(d) guidelines. State must have public hearings before Region can act on plan. State plans to hold and certify hearings in FY 80. State has 9 or 10 plants in 2 counties.[29]

B. EPA Region 6

1. Negative declaration received from New Mexico.[30]

2. Texas. Plan not submitted. State has several phosphate plants.[30]

3. Oklahoma. Plan not submitted. Region does not have information on whether State has phosphate plants.[30]

4. Arkansas. Draft plan submitted in July 1979. Goes to hearing in November 1979.[30]

5. Louisiana. Plan has been submitted. Plan generally met 111(d) guidelines except would allow emissions about 100 times guideline requirements for triple superphosphate (TSP). The reason given for allowing the higher TSP-plant emissions is that, because of hot weather, pond temperature is too high for more effective fluoride removal in scrubbers. The Region is considering suggesting that the State employ a contractor to study the claim that guidelines cannot be met, but has not yet acted.[30]

C. EPA Region 10

1. Idaho. Plan not submitted. An extension to July 1979 had been discussed, but was not formally requested.[31]

2. Idaho is the only state in Region 10 that has phosphate plants. [31]

D. No state plan has yet been approved by EPA. [32]

EPA guidelines for development of State emission standards are specified in the publication, "Final Guidelines Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants," U.S. EPA, Research Triangle Park, N.C., EPA-450/2-77-005, March 1977.

6.5 REFERENCES FOR SECTION 6.

1. Telecon. W. Herring, U.S. EPA OAQPS, to W. Aronson, U.S. EPA Region 4. April 17, 1979. Subject: Phosphate Industry in Region 4.

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6. Telecon. W. Herring to B. Varner, U.S. EPA Region 5. April 24, 1979. Subject: Phosphate Industry in Region 5.

7. Telecon. W. Herring to L. Szempruch, U.S. EPA Region 5. April 24, 1979. Subject: Phosphate Industry in Region 5.

8. Telecon. W. Herring to J. Hepola, U.S. EPA Region 6. May 21, 1979. Subject: Phosphate Industry in Region 6.

9. Telecon. W. Herring to S. Spruiell, U.S. EPA Region 6. June 5, 1979. Subject: Phosphate Industry in Region 6.

10. Telecon. W. Herring to J. Pfander, U.S. EPA Region 10. May 21, 1979. Subject: Phosphate Industry in Region 10.

11. Telecon. W. Herring to B. Swan, U.S. EPA Region 10. May 21, 1979. Subject: Phosphate Industry in Region 10.

12. Telecon. M. Johnson, U.S. EPA Region 10. May 22, 1979. Subject: Phosphate Industry in Region 10.

13. Telecon. W. Herring to J. Symes, State of Florida. April 23, 1979. Subject: Phosphate Industry in Florida.

14. Telecon. W. Herring to Derr Leonhardt, State of N.C. April 20, 1979. Subject: Phosphate Industry in N.C.

15. Telecon. W. Herring to J. Reed, State of Illinois. April 24, 1979. Subject: Phosphate Industry in Illinois.

16. Telecon. G. Wallin, State of Texas, to W. Herring. April 30, 1979. Subject: Phosphate Industry in Texas.

17. Telecon. W. Herring to O. Tanner, State of Louisiana. May 1, 1979. Subject: Phosphate Industry in Louisiana.

18. Telecon. W. Herring to R. Stenner, State of Idaho. April 19, 1979. Subject: Phosphate Industry in Idaho.

19. Letter and attachments from R. Stenner, State of Idaho, to W. Herring. April 20, 1979. Subject: Phosphate Industry in Idaho.

20. U.S. Patent. Direct Granulation Process for Triple Superphosphate. Assignee: J.R. Simplot Co. No. 4,101,637. July 18, 1978.

21. Letter and attachments from J.F. Cochrane, J.R. Simplot Co., to D.P. Dubois, EPA Region 10. December 30, 1977. Subject: TSP Performance Test.

22. Telecon. W. Herring, U.S. EPA OAQPS, to W. Aronson, U.S. EPA Region 4. April 18, 1979. Subject: Phosphate Industry in Region 4.

23. Environmental Impact Statement, Central Florida Phosphate Industry, Vol. 3. U.S. EPA Region 4. Atlanta, GA. Publication No. EPA 904/9-78-026c. Nov. 1978. p. 1-63.

24. Reference 23. p. 1-46.

25. Reference 23. p. 1-222.

26. Telecon. W. Herring to R. Stenner, State of Idaho. April 25, 1979. Subject: Phosphate Industry in Idaho.

27. Memo from J.S. Nader, EPA Environmental Sciences Research Laboratory, to G.B. Crane, EPA Emission Standards and Engineering Division. June 25, 1979. Subject: Status of Development of Continuous Monitor for Fluoride Emissions.

28. Memo from E. McCarley, EPA Emission Measurement Branch, to G.B. Crane. June 26, 1979. Subject: Report, Continuous Monitoring System for Fluoride Emissions from Stationary Sources.

29. Telecon. W. Bishop, EPA Region 4, to W. Herring. October 10, 1979. Subject: State Plans for Existing Phosphate Plants.

30. Telecon. W. Herring to J. Stubberfield, EPA Region 6. October 9, 1979. Subject: State Plans for Existing Phosphate Plants.

31. Telecon. K. Lepic, EPA Region 10, to W. Herring. October 11, 1979. Subject: State Plans for Existing Phosphate Plants.

32. Discussion. W. Herring with R. Shell, EPA Control Programs Development Division. October 9, 1979. Subject: State Plans for Existing Phosphate Plants.

7. CONCLUSIONS

7.1 HEMIHYDRATE PROCESS FOR WET PROCESS PHOSPHORIC ACID (WPPA)

The hemihydrate (hemidihydrate or HDH) process for WPPA production appears to have certain potential advantages for reducing fluoride air pollutant emissions, compared with the conventional dihydrate processes.

Fluorides evolved in process gases are recovered as byproduct fluosilicic acid (H_2SiF_6) at an efficiency reported to be greater than 99%. (Possible fluoride recovery between 65 and 99% is reported for the dihydrate process). Also, P_2O_5 recovery is reported to exceed 98%, which is alleged to be greater than in the dihydrate process. Greater P_2O_5 recovery would reduce the amount of phosphoric acid entering pond water. This reduction would tend to increase pond pH, and thereby further reduce fluoride emissions from ponds and improve scrubber efficiency.

Gypsum produced in the HDH process is reported to be of sufficient purity to be used in building material. This indicates that the gypsum may be substantially free of radioactive constituents and saleable. This is in contrast to dihydrate-process gypsum, which has radioactive constituents, and therefore is not saleable and must be retained at the plant in gypsum piles. The HDH process therefore might reduce gypsum piles and the attendant radioactive emissions and fugitive dust generated in handling the piles.

Possible disadvantages of the HDH process are that radioactive constituents removed from the gypsum would apparently go into the product WPPA or pond water. Also, recovery of valuable uranium from HDH product WPPA is reported less satisfactory than recovery from the more dilute WPPA produced in the dihydrate processes.

The HDH process has been used commercially in Europe and Japan but not in the U.S.

7.2 SIMPLOT PROCESS FOR GRANULATED TRIPLE SUPERPHOSPHATE (GTSP)

The new Simplot process, in which GTSP is made by treating limestone with WPPA, provides a means for reducing local fluoride emissions at the plant where it is applied. However, the fluoride emissions from the Simplot process added to those from the production of the WPPA, used in the Simplot process, might not be less than the corresponding total for the old process.

Emission test results for the Simplot process (0.187 lb F/ton P_2O_5) indicate that fluoride emissions comply with - but are not substantially less than - requirements of the present NSPS (0.20 lb F/ton P_2O_5).

The Simplot process appears to reduce or eliminate fugitive emissions and evolved fluorides during storage by eliminating the curing period required when GTSP is made from run-of-pile triple superphosphate (ROP).

7.3 WET GRINDING OF PHOSPHATE ROCK

Emissions of sulfur dioxide (SO_2) and dust with radioactive content, that occur during drying, grinding, and transport of phosphate rock, can be substantially reduced by eliminating rock drying prior to grinding and chemical processing.

Companies are converting from dry to wet grinding of phosphate rock to save energy.

7.4 SCRUBBING SYSTEMS, COOLING TOWERS, AND GYPSUM PONDS

Scrubbing systems remain the principal means of controlling fluoride emissions from phosphate plants. A few changes have been introduced since NSPS publication.

7.4.1 Fluoride Recovery

Scrubbers that recover fluorides as saleable H_2SiF_6 have been incorporated at a substantial number of WPPA plants. These scrubbers are reported to recover between 65 and 99% of the gaseous fluorides emitted during acidulation and acid concentration. Fluoride removal, by this means, substantially reduces the fluorides emitted from plant pond systems or cooling towers. Costs of fluoride recovery as H_2SiF_6 might exceed H_2SiF_6 market prices, but not to an extent that precludes its commercial applicability for reducing emissions.

7.4.2 Cooling Towers

Cooling towers are being used at a substantial number of plants in place of cooling ponds, or instead of the gypsum pond area required to cool water for scrubbers and barometric condensers. The cooling towers are used in closed-loop systems. Here, water from the scrubbers or barometric condensers goes to the cooling tower, where it is cooled - mainly by evaporation - to the required scrubbing temperature. The water is then returned to the scrubbers or barometric condensers, thus closing the cooling-tower loop. Make-up water is added to the closed loop from the gypsum pond water overflow caused by rainfall, or from the plant storm water collection system. Four variations of this cooling-tower closed loop system were identified in this investigation:

1. Cooling Tower without Fluoride Recovery and without Caustic Treatment

In a WPPA plant system, process gases are scrubbed, without prior removal of fluorides as byproduct H_2SiF_6. The resulting scrubbing water is cooled in a cooling tower, then returned to the scrubbers. The water in this closed loop is not caustic treated to increase its pH and limit fluoride emissions from the tower. Substantial fluoride emissions from the cooling tower probably occur in this system.

2. Cooling Tower with Fluoride Recovery but without Caustic Treatment

In a WPPA plant system, process gases are first scrubbed in a scrubber designed to recover fluorides as byproduct H_2SiF_6. The gases are then scrubbed again in the plant barometric condensers. The water from the barometric condensers is cooled in a cooling tower and returned to those condensers. This water is not caustic treated to limit fluoride emissions from the tower. Fluoride emissions from the cooling tower would be less in this system than in the system described in paragraph 1, above.

3. Cooling Towers with Fluoride Recovery and Caustic Treatment

A WPPA plant system that employs a cooling tower with fluoride recovery and caustic treatment is similar to that described in paragraph 2, above, except that the water in the cooling tower is treated with sodium hydroxide (NaOH) to increase its pH and limit fluoride emissions from the tower. Also, a slip stream of water from the tower is limed to precipitate the fluoride and regenerate the NaOH. Fluoride emissions

from the cooling tower would be less in this system than in either of the systems described in paragraphs 1 or 2, above.

4. Cooling Tower with Nitrogen and Phosphorous Recovery and with Caustic Treatment

In a diammounium phosphate (DAP) plant system, process gases are first scrubbed with dilute phosphoric acid to recover ammonia and phosphorous compounds. To remove fluorides, the gases are then scrubbed again with water that is treated with NaOH in a cooling-tower closed-loop system. A slip stream of water from the tower is limed to precipitate the fluoride and regenerate the NaOH. Fluoride emissions from the cooling tower would be reduced to a very low rate in this system.

7.5 FLUORIDE EMISSION MONITORING

A system that would satisfactorily monitor fluoride emissions has not been developed. However, the present NSPS for phosphate plants requires continuous monitoring of total pressure drop across the process scrubbing system. It is thus required that records be kept of when emission control systems are operated and not operated.

7.6 RADIOACTIVE EMISSIONS

The health impact of radioactive emissions from phosphate plants is being studied by the EPA Office of Radiation Programs (ORP). Results of this study will determine whether those emissions will be listed as hazardous pollutants under Section 112 of the Clean Air Act. If these emissions are so listed, standards for their control will be developed by ORP, under Section 112.

7.7 AREAS FOR RESEARCH AND DEVELOPMENT

As noted above, phosphate plant pond area and pond fluoride emissions may be reduced by a WPPA plant system that includes: fluoride recovery as byproduct H_2SiF_6, and a closed-loop cooling tower system where scrubbing water is caustic treated, and a slip stream is limed to recover the caustic and precipitate the fluorides. This system is used, however, at only one plant, and its user reports difficulties which that company is working to overcome. Furthermore, the developer of this system, Dr. Aaron Teller, advocates a different system for future application. Dr. Teller's preferred system would use a baghouse with continuous injection of a dry additive that would remove fluorides by adsorption and filtration. Advantages claimed for this dry system include reduced pond area, reduced pond emissions, reduced plumbing costs, and reduced corrosion. Dr. Teller estimates pond cost at $2000 to $2500 per acre year, and plumbing costs at $1000 per foot of piping.[1]

The dry Teller system has not yet been used at a commercial phosphate plant. Two such units are being furnished to the IMC New Wales, Fla., plant. These units will be applied to GTSP and DAP processes. They are expected to be on line by 1980.[1]

The dry continuous-injection baghouse described above might provide an improved emission control system for phosphate plants, compared with scrubbing systems now in use.

7.8 INDUSTRY GROWTH

Some processes are being improved, and there is some new construction of phosphate fertilizer plants in the U.S. Particularly notable also are (1) conversions from processing dry phosphate rock to processing wet

are (1) conversions from processing dry phosphate rock to processing wet rock and (2) conversions from process cooling water ponds to cooling towers.

The responses obtained in this investigation to enquiries to EPA Regional offices and State agencies indicate that the extent of new source construction is moderate. Furthermore, industry growth to 1985 will probably also be moderate.

7.9 REGULATION OF EXISTING SOURCES

Only two states - Florida and Louisiana - had submitted formal Section 111(d) plans for controlling fluoride emissions from existing phosphate plants by October 1979. Both of these plans have less stringent requirements than those of the EPA guidelines. One state - Arkansas - had submitted a Section 111(d) draft plan. No state plan had been approved by EPA.

7.10 REFERENCES FOR SECTION 7.

1. Memo from G.B. Crane, EPA Emission Standards and Engineering Division, to File. 5/15/79. Subject: Review of Phosphate Fertilizer NSPS: Conversation with Dr. Aaron Teller.

8. RECOMMENDATIONS

8.1 HEMIHYDRATE PROCESS FOR WET PROCESS PHOSPHORIC ACID (WPPA)

The hemihydrate (HDH) process is not recommended for study as a possible basis for NSPS revision because there are no commercial HDH plants in the U.S. and because no data showing reduced emissions were found in this investigation. However, reported reduced energy consumption and reduced capital cost might lead to commercial use of this process in the U.S. In the event of commercial adoption, this matter should be reconsidered.

8.2 SIMPLOT PROCESS FOR GRANULATED TRIPLE SUPERPHOSPHATE (GTSP)

The Simplot process is not recommended for study as a possible basis for NSPS revision because available data do not show that it effects a substantial reduction of process emissions below the present NSPS requirement. This process should, however, be included in any future study concerned with regulating evolved-fluoride or fugitive emissions from GTSP storage facilities.

8.3 WET GRINDING OF PHOSPHATE ROCK

Wet grinding is not recommended for study as a possible basis for NSPS revision because the energy-saving advantage of this process modification is presently inducing companies to adopt it.

8.4 SCRUBBING SYSTEMS, COOLING TOWERS, AND GYPSUM PONDS

8.4.1 Fluoride Recovery

Fluoride recovery, as byproduct H_2SiF_6, is recommended for inclusion if a study is undertaken to determine a basis for NSPS revision.

8.4.2 Cooling Towers

Cooling towers are recommended for inclusion if a study is undertaken to determine a basis for NSPS revision.

8.5 RADIOACTIVE EMISSIONS

Findings of the Office of Radiation Programs study of radioactive phosphate plant emissions should be obtained if a study is undertaken to determine a basis for NSPS revision. This information would be needed to show impacts of proposed NSPS revisions on radioactive emissions.

8.6 RECOMMENDATION ON NSPS REVISION STUDY

Because there have been no significant improvements in fluoride removal efficiencies by aqueous scrubbing, or no demonstrations of emerging technologies for fluoride control, a study to establish a basis for NSPS revision is not recommended now. Possible revision should be reconsidered in four years, by which time some new control technologies may have been proven.